DISSOCIATION KINETICS OF DIATOMIC MOLECULES
IN THE ABSENCE OF VIBRATIONAL EQUILIBRIUM

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ABSTRACT   *2₉739*

To account for the dissociation of diatomic molecules under the
variable temperature conditions typical of aerodynamic problems,
the vibrational relaxation occurring in this case is approxi-
mately analyzed from the energy point of view at low tempera-
tures, when the departure from vibrational equilibrium is only
slight, and at high temperatures, when this departure becomes
significant. The effect of vibrational relaxation vanishes when

1) the vibrational relaxation time shrinks to zero at low
temperatures (equilibrium of vibrational degrees of freedom);

2) the temperature becomes very high.

The rate of dissociation is usually calculated by analyzing a molecule /376*

situated in a heat bath at constant temperature T. For a number of applications,
however (for example, in high-velocity aerodynamics), the case when the temper-
ature does not remain constant becomes important. Rapid variations in tempera-
ture can cause equilibrium to be upset with regard to the internal degrees of
freedom of the dissociating molecule. This leads to the question of relaxation
of the internal degrees of freedom and its effect on the rate of molecular
dissociation.

Aerodynamics is concerned mostly with diatomic molecules, hence we will
restrict our discussion to this case. It is of practical importance to consider

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*Numbers in the margin indicate pagination in the original foreign text.

the relaxation of vibrations; the rotational relaxation time of almost all molecules is so small that the rotation may be regarded as in equilibrium in the problems of interest in the theory of continuous media.

Some estimates are given below for the influence of vibrational relaxation on the rate of dissociation.

1. Let us consider first the case when the deviations of the vibrations from equilibrium are insignificant. This case occurs when the temperature T is not very high, so that the total internal energy of the molecule is considerably less than the dissociation energy D. Otherwise there occur sizable violations of the vibrational equilibrium due to the increased dissociation rate (ref. 1).

According to some estimates (e.g., ref. 2), one would expect (in the case of identical molecules) the exchange of vibrational energy to proceed much more rapidly than the transformation of translational and rotational kinetic energy into vibrational energy. This means that the vibrational distribution function will have a Boltzmann configuration with temperature T^1 (t) differing from the translational temperature T. Assuming that the dissociation from each level proceeds independently and that the main contribution to dissociation comes from m levels situated sufficiently near the dissociation limit, such that the transitions from these levels to a continuous spectrum may be assumed approximately equally probable, we find

$$\frac{k^1}{k} = \frac{1}{m} \frac{f(T)}{f(T^1)} f^m(\theta),$$ (1)

where $f(T)$ is vibrational statsum; $f^m(T) = \sum_{l=N-m}^{N-1} e^{-E_l/KT}$; $\frac{1}{\theta} = \frac{1}{T^1} - \frac{1}{T}$; N is the number of molecular levels. Equation (1) was derived on the assumption that only the relative motion of the molecules along the centerline contributes to

dissociation. Inclusion of the other degrees of freedom can be accomplished quite easily within the framework of statistical theory (ref. 3).

Assuming that the difference between T and T^1 is small and introducing the notation $\Delta = \dfrac{T - T^1}{T}$, we obtain

$$\frac{k^1}{k} \approx 1 + \frac{E(T) - \bar{E}_m}{KT} \Delta, \tag{2}$$

where $E(T) = \dfrac{1}{f(T)} \displaystyle\sum_{i=0}^{N-1} E_i e^{-E_i/KT}$ and $\bar{E}_m$ is the arithmetic mean of the vibrational energy in the interval $(N - m, N)$.

On the other hand, from the vibrational relaxation equation

$$\frac{dT^1}{dt} = \frac{T^1 - T}{\tau_k} \tag{3}$$

(τ_k is the vibrational relaxation time) we obtain, for small deviations from equilibrium, $\Delta = \tau_k/\tau_0$, where $\tau_0 = T \left|\dfrac{dT}{dt}\right|^{-1}$ is the characteristic fluctuation time of the translational temperature. Consequently,

$$\frac{k^1}{k} \approx 1 - C\,\frac{\tau_k}{\tau_0}, \tag{4}$$

where the temperature function $C > 0$ can be determined once the specific molecular model is decided. Clearly, the effect vanishes when $\tau_k/\tau_0 \rightarrow 0$ $(T^1 \rightarrow T)$.

2. Let us estimate the maximum effect that will result from vibrational nonequilibrium. We will suppose that the distribution function is

$$f_i = \begin{cases} 0 & i \neq 0 \\ 1 & i = 0. \end{cases} \tag{5}$$

From this, simple computations yield

$$\frac{k^1}{k} = \frac{f(T)}{N}. \tag{6}$$

The right-hand side of (6) is less than one for all finite temperatures and tends to unity as $T \to \infty$.

Consequently, the effect vanishes in the limiting case of very high temperatures.

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